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(54) Title: COEXTRUDED MULTILAYER FOAMED FILM FOR PLASTIC CONTAINER CLOSURES AND PROCESS FOR MANUFACTURE

(57) Abstract

A plastic container closure, such as a bottle cap liner or tamper evident seal, is formed from a coextruded multilayer foamed film. The coextruded multilayer foamed film has at least one solid film layer of a first polyolefin blend containing linear low density polyethylene, low density polyethylene, and, optionally high density polyethylene, and at least one foamed layer of a second polyolefin blend containing linear low density polyethylene, low density polyethylene, and optionally ethylene vinyl acetate. The multilayer foamed film may be coextruded using a blown film or cast film extrusion process under defined conditions. The coextruded multilayer foamed film may be laminated to other materials such as polyester film, thermoplastic adhesive films or metallic films and used as a plastic container closure, or may be applied as a liner to a plastic bottle cap.

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COEXTRUDED MULTILAYER FOAMED FILM FOR PLASTIC CONTAINER
CLOSURES AND PROCESS FOR MANUFACTURE

The present invention relates to plastic container closures, such as bottle cap liners and tamper evident seals, formed from a coextruded multilayer 5 foamed film, to coextruded multilayer foamed films which are useful for plastic container closures, and to a method for coextruding such multilayer foamed films.

In a number of industries tamper evident seals 10 are applied over plastic container openings for security purposes. Because of the container contents some of those industries also require that the seal keep liquid contents from leaking from the container, and/or keep air and contaminants from invading the container, and 15 yet be easily removable. Industries having these requirements include the milk, orange juice, and motor oil industry. Common paper, foil, and paper-foil seals are often inadequate for use in those applications since 20 they do not afford the quality of seal desired and since they are not easily applied by induction or high frequency sealing equipment.

Likewise, such seals are often inadequate when 25 used as liners for threaded and snap-on bottle caps. In

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those instances a greater degree of compression is needed in the liner than is commonly found in paper, foil, and paper-foil seals.

Accordingly, other forms of plastic container 5 closures have been developed. For example, it is known to use a single layer of a 5 to 10 mil (0.127 to 0.254 mm) thick closed-cell high density polyethylene (HDPE) foam film. However, such single foam layers are 10 fragile, do not possess sufficient sealing properties for many uses and must be laminated to a metal foil and/or polyester film prior to being applied to the plastic container. Even then a number of disadvantages remain.

15 It has recently been suggested that a layer of compressible polyolefin foam may be adhered to a solid polymeric film to produce a liner suitable for a bottle cap. Thus in U.S. Patent No. 4,818,577, assigned to 20 Minnesota Mining and Manufacturing Co., there is disclosed a bottle cap liner which has a layer of compressible polyolefin foam, a layer of adhesive, and a layer of polymeric film such as polyester, silicone, polytetrafluoroethylene, and polyimide film. While such 25 a multilayer foam/film is an improvement over a single foam layer, problems exist in the lamination process and still, as mentioned above, a number of disadvantages remain with laminated materials.

30 Finally, it is also known to use coextruded multilayer foamed films as plastic container closures. Thus, Tri-Seal International, Inc. of Blauvelt, New York has recently introduced its Tri-Seal F-828 liners which are a 20 to 60 mil (0.51 to 1.5 mm) thick three-ply coextruded foamed polypropylene core between two facings

of solid polypropylene. The solid polypropylene film facings are said to protect the container contents from penetration and evaporation while the foamed plastic core is said to be resilient, compressible, and resistant to foam collapse. The Tri-Seal F-828 liners 5 are also said to be capable of radially expanding under pressure should they be used with plastic or metal bottle caps. Still, because of their relative thickness, applicability is limited. U.S. Patent Nos. 10 4,107,247 and 4,206,165 assigned to Tri-Seal International, are believed to cover the method of coextruding such multilayer foamed film liners.

Other methods for coextruding multilayer foamed 15 films are also known. For example, U.S. Patent No. 3,557,265, assigned to the assignee of the present invention, discloses a method of extruding laminates whereby optionally alternating foamed and unfoamed layers may be obtained. See also U.S. Patent Nos. 20 4,022,858 and 3,553,070, assigned to Mobil. More recently, U.S. Patent Nos. 4,533,578 and 4,657,811 to Mobil disclose coextrusion methods for producing a relatively thin three-layer polyolefin film having a foamed middle layer. The coextruded multilayer foamed 25 film is adapted for use in high performance polyolefin trash bags. The outer facing layers are linear low density polyethylene (LLDPE) or high density polyethylene (HDPE) and the foam core is a low density polyethylene (LDPE). Finally Published German Patent 30 Application DE 3722139 dated January 19, 1989, assigned to Stoll Kunststoffe, discloses producing a thermo-plastic foamed film particularly for carrier bags and packaging bags by coextruding at least two layers (which may be polyolefin), one containing a blowing agent and

one containing no blowing agent. The final thickness of the individual layers is 6 to 18, and preferably 12, microns. There is no suggestion in these later patents that such foamed films could be used as plastic container closures, nor as a practical matter could they 5 be effectively so used.

Thus while considerable technology exists in the foamed film area, to date it has not yet been possible to produce a plastic container closure which 10 satisfies all of the needs of the industries which package their contents in plastic containers (bottles, jars, and jugs). In particular, the need exists for a relatively thin (less than about 10 mils (0.254 mm) 15 total thickness) multilayer foamed film which has at least one solid layer for overall strength and barrier resistance and a foamed layer which is as strong as possible while still having the desired degree of resilience and compressibility such that it can be used 20 for a plastic container closure. The need also exists for an effective method of producing such multilayer foamed films.

The present invention provides an efficient 25 method of coextruding a 3 to 10 mil (0.08 to 0.25 mm) thick multilayer foamed film which can be used for plastic container closures, a unique coextruded multilayer foamed film, and plastic container closures 30 formed from that coextruded multilayer foamed film.

The plastic container closures of the present invention can be formed from the thin, coextruded multilayer foamed film. Preferably the plastic container closure is in one of two forms. Thus, the plastic container closure of the present invention may

be a laminate of the multilayer foamed film adhered to an additional layer or layers such as a polyester film, thermoplastic adhesive film, metallic foil or all three so that the laminate is high frequency sealable over the opening of a plastic container. Alternative, the 5 plastic container closure of the present invention may be formed from the multilayer foamed film (or laminate thereof) and a threaded or snap-on bottle cap where the multilayer foamed film (or laminate thereof) is attached 10 to the bottle cap as a liner so that it can be compression or pressure applied to the opening of a plastic container.

The multilayer foamed film has at least one 15 solid polyolefin film layer which is preferably a first polyolefin blend and at least one foamed polyolefin layer which is preferably a second polyolefin blend. The first polyolefin blend of the solid film layer contains linear low density polyethylene (LLDPE) and low 20 density polyethylene (LDPE). The first polyolefin blend may also contain high density polyethylene (HDPE). The LLDPE gives the resultant solid polyolefin film layer strength, the HDPE modulus, and the LDPE better 25 processing characteristics. Preferably the first polyolefin blend of the solid film layer contains 20 to 90 percent LLDPE, 10 to 90 percent LDPE, and 0 to 90 percent HDPE, more preferably 10 to 80 percent LLDPE, 10 to 60 percent LDPE, and 0 to 50 percent HDPE, and most 30 preferably 50 percent LLDPE, 20 percent LDPE and 30 percent HDPE. Additional materials such as inorganic fillers, pigments, antioxidants or UV stabilizers, fire retardants, etc. can be added.

Such additional materials can also be added to the second polyolefin blend of the foamed layer. The

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second polyolefin blend also contains LLDPE and LDPE. Again the LLDPE improves the physical properties and strength characteristics and the LDPE acts as a melt processing aid to assist in the extrusion process and works to maintain melt strength. The second polyolefin 5 blend of the foamed layer may also contain ethylene vinyl acetate (EVA) which improves melt strength and tear resistance. Optionally, some HDPE may be included; although, that is generally to be avoided because the 10 addition of HDPE in the foamed layer greatly decreases tear strength. Prior to extrusion processing the second polyolefin blend will also include a chemical blowing agent such as azodicarbonamide or sodium bicarbonate/citric acid. Preferably the second 15 polyolefin blend prior to processing contains 10 to 90 percent LLDPE, 10 to 90 percent LDPE, 0 to 50 percent EVA, 0 to 30 percent HDPE, and 0.1 to 1 percent blowing agent, more preferably 40 to 75 percent LLDPE, 20 to 60 percent LDPE, 2 to 10 percent EVA, and 0.1 to 1 percent 20 blowing agent, and most preferably about 60 percent LLDPE, 35 percent LDPE, 5 percent EVA, and 0.1 to 1 percent blowing agent. The blowing agent, of course, will form the primarily closed cell foam structure 25 during the melt extrusion process and will not exist as such in the resulting foamed layer of the multilayer foamed film.

Preferably the coextruded multilayer foamed 30 film is either a two-ply or a three-ply film. Coextrusion of a foamed polyolefin layer with at least one solid polyolefin film layer is needed in order to obtain overall composite strength. In a two-ply coextruded film preferably 10 to 40 percent of the total film thickness will consist of the solid polyolefin film

layer and 90 to 60 percent will consist of the foamed polyolefin layer. In a three-ply coextruded film, there are preferably two outer solid polyolefin film layers which constitute 5 to 20 percent of the film thickness and a middle foamed polyolefin layer which is 90 to 60 percent. It is also possible to have a three-ply coextruded film with two outer foamed polyolefin layers and a middle solid polyolefin film layer.

It is, thus, possible to vary the arrangement and/or thicknesses of the respective layers and/or the respective polyolefin blends of the respective layers within the parameters given to produce a coextruded multilayer foamed film particularly suited to use for a plastic container closure. By varying the LLDPE:HDPE ratio in the solid polyolefin film layer, desired strength and tear properties (LLDPE) versus modulus (HDPE) can be obtained. Likewise, by using large amounts of LLDPE in the foamed polyolefin layer maximum strength characteristics are obtained.

The method of coextrusion is also important in producing a multilayer foamed film particularly well suited for use for plastic container closures. Either a blown film (tubular bubble) or cast film (slot die) extrusion process may be used. But, in either instance, foam extrusion melt temperature control is important to control foam cell size. Small cells tend to give the strongest physical properties (tensile strength, tear strength, film ultimate elongation) while larger sized foam cells will deteriorate the film properties. Melt temperatures that are excessively high will cause large cell size formation (and result poor physical properties). Conversely, foam layer melt temperature that are too low will not completely activate the

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chemical blowing agent and will result in incomplete foam expansion and die-lip buildup of solid blowing agent residue. Preferably the extrusion temperature is approximately 204°C to 232°C.

5 The size of the die gap is also important. A large die gap will result in low extrusion back pressure and will allow for premature foaming. This will result in poor foam properties, generally caused by large cell size and the presence of open cells. Decreasing of the
10 die gap will result in an increase in extrusion pressure which will keep the blowing agent in solution in the polymer melt. The resulting foam exhibits desired small sized, closed cell foam, which provides for the
15 strongest physical properties. Preferably the die gap is less than 50 mils (1.27 mm) and most preferably is 20 to 40 mils (0.51 to 1.02 mm).

20 The result is a multilayer foamed film having properties which make it particularly well suited for a plastic container closure. A key is that the resulting foamed polyolefin layer has an average cell size of less than 0.6 millimeters in length and most often less than 0.4 millimeters in length. An average cell size of less
25 than 0.6 millimeters in length is desirable in that above that size, the foamed polyolefin layer has insufficient tensile strength, tear strength, and impact strength to provide a multilayer foamed film usable for plastic container closures. Thus, with an average cell
30 size of less than 0.6 millimeters in length the foamed polyolefin layer (and resulting multilayer foamed film) is capable of forming an adequate compression seal when used as a liner for a threaded or snap-on bottle cap.

The multilayer foamed film may also be laminated to aluminum foil, polyester film and/or thermoplastic adhesive film, and then thermally sealed to the mouth of liquid containing plastic bottles (milk jugs, juice bottles, engine oil bottles, cleaning agent bottles, etc.) to prevent the liquid contents from spilling out during initial transportation and storage and to provide a safety tamper evident seal on a bottle. In this alternate form, the preferred configuration is a multilayer foamed film having a polyester film (preferably a polyethylene terephthalate film) and a metallic foil joined to one surface of the multilayer foamed film with a thermoplastic or thermosetting adhesive (including aqueous or solvent based adhesives) and, most preferably, also having a polyester film joined to the other surface with a similar adhesive. The metallic foil, which is preferably on aluminum foil, may have a Surlyn overcoat for protection purposes.

Accordingly, the present invention provides a new and improved plastic container closure, a unique coextruded multilayer foamed film which is particularly useful for a plastic container closure, and a novel method of coextruding such a multilayer foamed film. The advantages of the invention will be apparent from the following detailed description of the invention and the appended claims.

Preferably the coextruded multilayer foamed film of the present invention contains two plies, having one solid polyolefin film layer and one foamed polyolefin layer, or three plies which preferably has two outer solid polyolefin film layers and a middle foamed polyolefin layer, although, it may have two outer

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foamed polyolefin layers and a middle solid polyolefin film layer.

The preferred composition of the foamed polyolefin layer is a blend of LLDPE, LDPE and optionally 5 EVA. The solid polyolefin film layer contains LLDPE and LDPE, and optionally HDPE. The foamed polyolefin layer has small closed cells having an average cell size of less than 0.6 millimeters in length and preferably less than 0.4 millimeters in length. Such a foamed 10 polyolefin layer can be created with the method of the present invention by use of a solid chemical blowing agent which decomposes at prescribed extrusion temperatures liberating gases which expand the molten 15 polymer.

The use of solid chemical blowing agents (rather than physical blowing agents such as chlorofluorocarbons or other direct injection of gases) 20 permit the present multilayered foamed films to be made on conventional film production equipment. In practice, it has been found that sodium bicarbonate/citric acid blend chemical blowing agents (available as Hydrocerol from Boehringer Ingelheim, distributed by Henley 25 Chemicals, Inc. or as a concentrate in LDPE from Quantum/USI) give smaller cell size than, for example, azodicarbonamide chemical blowing agents. Thus, the preferred blowing agent for the disclosed foamed film 30 utilizes Hydrocerol-based blowing agent concentrates although others such as azodicarbonamide, 5-phenyl tetrazole, sodium borohydride, sulfonyl hydrazides, etc. may be used.

The multilayered foamed film of the present invention will have a density or specific gravity less

than that of the base polymer or that of a comparable solid film. Coextruded two-ply and three-ply foamed films with densities of 0.65 to 0.80 g/cm³ are possible. The density of a typical solid polyethylene film would be approximately 0.92 g/cm³.

5

Both the two-ply and three-ply version of the instant coextruded multilayer foamed film can be produced either by known blown film (tubular bubble) or cast film (slot die) extrusion processes. As stated 10 earlier, foam extrusion temperature is important in determining foam cell size (and thus the resulting properties). The sodium bicarbonate/citric acid chemical blowing agent preferentially used decomposes 15 between 160°C to 204°C. Therefore, extrusion melt temperatures of at least 204°C must be experienced by the foam layer. Temperatures above 238°C, however, have been found to create large foam cells, which is detrimental to physical properties. Accordingly, the 20 preferred temperature range is approximately 204°C to 232°C.

As stated earlier, die gap is also an important equipment parameter for determining cell size. It has 25 been found that when coextruding a multilayered foamed film on a 6 inch (15 cm) diameter blown film line, a 80 mil (2 mm) die gap produced very large cells, while a 40 mil (1 mm) die gap yielded foam with small cells. A production plant trial on an 18 inch (45.7 cm) diameter 30 die with a 55 mil (1.4 mm) gap yielded unacceptably large celled foam. After changing the die gap to 40 mils (1 mm), good quality foam was made. Another production plant blown film trial on an 18 inch (45.7 cm) diameter die with 27 mil (0.7 mm) die gap yielded good quality (small cell size) 6.5 mil (0.17 mm)

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coextruded two-ply foamed film. It is thus preferred to run on a small die gap blown film line. Dies with 27 (0.7 mm) and 40 mils (1 mm) are known to produce small cell size foam. Dies with 55 (1.4 mm) and 80 mil (2 mm) die gaps have been found to produce excessively large 5 cells. Accordingly a die gap of less than 50 mils (1.27 mm) and desirably between 20 and 40 mils (0.5 mm to 1.0 mm) is preferred.

10 Example 1

A two-ply coextruded multilayer foamed film was made on a blown film line. The solid layer composition and foam layer composition are provided below.

15 The coextruded film was extruded with a 30 percent solid layer (30 percent solid layer of total film gauge) at a total gauge of 6.5 mils (0.17 mm). Extrusion conditions for the Egan 2 1/2 inch (6.35 cm) 24:1 L/D extruder (foam layer), Egan 1 1/2 inch (3.8 cm) 20 24:1 L/D extruder (solid layer) and Uniflo 6 inch (15 cm) diameter die with 40 mil (1 mm) die gap are given:

25

The physical properties of the 6.5 mil (0.17 mm) 2-layer foam film are shown below for the machine direction (MD) and transverse direction (TD) orientations of the film.

30 The film had a 0.76 g/cm^3 overall specific gravity (density) and had an average MD cell length of 0.3mm and a TD cell width of 0.2 mm.

Example 2

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	<u>Solid Layer</u>	<u>Foam Layer</u>
	60% DOWLEX LLDPE 2045 (1)	60% DOWLEX LLDPE 2045 (1)
	30% Dow HDPE 61513.01 (1)	35% Dow LLDPE 681 (1)
5	10% Dow LDPE 681 (1)	5% DuPont Elvax 3190 EVA (3)
	10 phr Ampacet 11560 White (2)	4 phr Spectratech FM 1764L (4)

Note: phr means parts per hundred

10 (1) Available from The Dow Chemical Company, Midland, Michigan, assignee of the present invention.

(2) A titanium dioxide pigment available from Ampacet Corp., Mt. Vernon, NY.

15 (3) Available from E.I. DuPont de Nemours, Wilmington, Delaware.

(4) The foam concentrate, Spectratech FM1764L, which is a 10 percent Hydrocerol (sodium bicarbonate/citric acid blend) blowing agent in LDPE

20 concentrate manufactured by Quantum/USI, was utilized at four parts per hundred parts of resin (phr).

A two-ply multilayer foamed film with a higher level of HDPE and lower LLDPE level in the skin layer and lower level of LLDPE in the foamed layer than that of Example 1 was made as a blown film using identical conditions as stated previously. The overall film modulus was higher (stiffer film) and the tensile strength slightly greater, but MD tear strength was significantly reduced over the film composition given above.

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		<u>SOLID LAYER EXTRUDER</u>	<u>FOAM LAYER EXTRUDER</u>	<u>DIE</u>
	Screw Speed (rpm)	140	40	All Die zones (°C) 380
5	Pressure (psig) (kg/cm ²)	3700 (259)	4800 (336)	Die lip zone (°C) 400
	Barrel Zone 1 (°C)	171	171	
10	Barrel Zone 2 (°C)	188	199	
	Barrel Zone 2 (°C)	204	210	
15	Adapter Zone (°C)	204	210	
	Transfer Line (°C)	204	210	
	Polymer Melt Temp (°C)	229	231	
20	Line Speed (fpm) (meters pm)	17 (5.2)		

		<u>MD</u>	<u>TD</u>
25	Ultimate Tensile Strength (psi) (kg/cm ²)	2320 (162.4)	1480 (103.6)
	Ultimate Elongation (%)	610	425
	2% Secant Modulus (psi) (kg/cm ²)	23,600 (1652)	25,200 (1764)
30	Elmendorf Tear Strength (g/mil)*	355	425
	Gull Wing Tear Strength (lb/in) (kgs/2.54cm)	535 (242.7)	540 (244.9)

*(1 mil = 0.0254 mm)

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	<u>Solid Layer</u>	<u>Foam Layer</u>
	45% DOWLEX 2045 (1)	50% DOWLEX 2045 (1)
5	45% Dow HDPE 61513.01 (1)	45% Dow LDPE 681 (1)
	10% Dow LDPE 681 (1)	5% DuPont Elvax 3190 (3)
	10 phr Ampacet 11560 (2)	4 phr FM 1764 (4)
10	1) Available from The Dow Chemical Company, Midland, Michigan, assignee of the present invention.	
	2) A titanium dioxide pigment available from Ampacet Corp., Mt. Vernon, NY.	
	3) Available from E.I. DuPont de Nemours, Wilmington, Delaware.	
15	4) The foam concentrate, Spectratech FM1764L, which is a 10 percent Hydroceral (sodium bicarbonate/citric acid blend) blowing agent in LDPE concentrate manufactured by Quantum/USI, was utilized at four parts per hundred parts of resin (phr).	
20		

		<u>MD</u>	<u>TD</u>
	Ultimate Tensile Strength (psi) (kg/cm ²)	2510 (175.7)	1350 (94.5)
25	Ultimate Elongation (%)	630	430
	2% Secant Modulus (psi) (kg/cm ²)	26,800 (1876)	26,900 (1883)
	Elmendorf Tear Strength (0.0254 mm)	250	400
30	Gull Wing Tear Strength (lb/in) (kg/2.54 cm)	205 (93)	210 (95.3)

Film Density = 0.76 g/cm³; MD cell length = 0.3 mm

Example 3

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A monolayer foam film was made on this 6" diameter blown film line (40 mil gap) using the same foam composition as used in Example 1. This trial was run to determine the physical properties of the foam by itself. Extrusion conditions were identical to those given in Example 1. A 4 mil (0.1 mm) monolayer foam was made to simulate the approximately 4 mils (0.1 mm) of foam that are contained in the 6.5 mil (0.17 mm) coextruded structure (30 percent solid layer in 6.5 mils (0.17 mm); therefore, 4.6 mils (0.12 mm) of foam, 1.9 mils (0.05 mm) of solid layer). In addition, a 6 mil (0.15 mm) monolayer foam film of the same composition was also made. To determine the physical properties of a solid layer, a 1.7 mil (0.04 mm) monolayer solid film with the same LLDPE-LDPE-EVA-TiO₂ composition as the solid layer of the coex film in Example 1 was also made via a blown film process under similar conditions as those given in Example 1.

Both monolayer foams exhibited very low MD tear strengths (less than 30 g/mil), low tensile strength (less than 1800 psi), and a low secant modulus (less than 15,000 psi). The monolayer solid film, on the other hand, exhibited significantly superior tensile strength and tear strength and a much higher 2 percent secant modulus than either of the foams. The 4 mil foam exhibited a 0.50 g/cm³ density, the 6 mil had a 0.62 g/cm³ density, and the solid film was based on a 0.96 g/cm³ density. Thus, the solid layer of the coex foam film (such as in Example 1) does provide the major strength characteristics of the composites, while the foam decreases the overall coex film density.

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MD FILM PROPERTIES

		4 MIL (0.1 mm) <u>FOAM</u>	6 MIL (0.15 mm) <u>FOAM</u>	1.7 MIL (0.04 mm) <u>SOLID</u> <u>FILM</u>
5	Ultimate Tensile Strength (psi) (kg/cm ²)	1410 (98.7)	1720 (120.4)	3740 (261.8)
10	Ultimate Elongation (%)	395	500	580
	2% Secant Modulus (psi) (kg/cm ²)	12,400 (868)	14,700 (1029)	38,200 (2674)
15	Elmendorf Tear Strength (g/mil) (0.0254 mm)	15	30	170
	Film Density (g/cm ³) 0.96	0.50	0.62	
20	MD Cell Length (mm)	0.6-0.8	0.5	--

Example 4

A series of three-ply coextruded multilayer foamed films (solid skins, foam core) were made to determine the effect of low and high ratios of LLDPE-HDPE in the skin and low and high ratios of LLDPE:LDPE in the foam core. The three-ply films were made on a 3-layer blown coextrusion film line with 6" diameter die and 40 mil die gap. Extrusion conditions are similar to those given previously. The three-ply films were 6 mils in gauge and exhibited constant overall densities of approximately 0.72 g/cm³.

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	<u>Solid Skin Layers (A)</u>	<u>Foam Core Layer (B)</u>
Film 4a	70% HDPE 07065 (1) 20% LLDPE 2045 (1) 10% LDPE 681 (1)	50% LLDPE 2045 (1) 45% LDPE 132 (1) 5% EVA 3190 (3) 4 phr FM 1764L (4)
5		
Film 4b	20% HDPE 07065 (1) 70% LLDPE 2045 (1) 10% LDPE 681 (1)	Same as 4a (B)
10		
Film 4c	45% HDPE 07065 (1) 45% LLDPE 2045 (1) 10% LDPE 681 (1)	20% LLDPE 2045 (1) 75% LDPE 132 (1) 5% EVA 3190 (3) 4 phr FM 1764L (4)
15		
Film 4d	Same as 4c (A)	75% LLDPE 2045 (1) 20% LDPE 132 (1) 5% EVA 3190 (3) 4 phr FM 1764L (4)
20		

1) Available from The Dow Chemical Company,
Midland, Michigan, assignee of the present
25 invention.

3) Available from E.I. duPont de Nemours,
Wilmington, Delaware.

4) The foam concentrate, Spectratech FM1764L, which
is a 10 percent Hydroceral (sodium
30 bicarbonate/citric acid blend) blowing agent in
LDPE concentrate manufactured by Quantum/USI, was
utilized at four parts per hundred parts of resin
(phr).

Physical properties for these films are shown below:

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MD Film Physical Properties

		<u>4a</u>	<u>4b</u>	<u>4c</u>	<u>4d</u>
5	Ultimate Tensile Strength (psi)(kg/cm ²)	2385 (167)	2285 (160)	2370 (166)	2190 (153)
	Ultimate Elongation (%)	570	565	555	595
	2% Secant Modulus (psi)(kg/cm ²)	36,400 (2548)	23,900 (1673)	27,000 (1890)	29,300 (2051)
10	Elmendorf Tear Strength (g/0.0254 mm)	35	195	60	175

Thus, the three-ply film with high level of HDPE in the skin layer (4a) had a higher modulus, but lower tear strength than the film with a high level of LLDPE (and low HDPE level) (4b). The film with the highest LLDPE level in the foam core (4d) had a higher tear strength than the film with the higher ratio of LDPE (4c). The film modulus of the two films which had a constant skin composition (4c and 4c) maintained a relatively constant secant modulus. The two films in which the skin HDPE:LLDPE ratio was varied (4a and 4b) showed a dramatic change in modulus with respect to HDPE level.

25 Example 5

30 A three-ply 5.7 mil (0.14) multilayer foamed film was made using a cast film (slot die) extrusion (40 mil (1 mm) gap) onto a chilled roll. Extrusion conditions and resulting film properties are given below:

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	<u>Skin Layer (A)</u>	<u>Foam Layer (B)</u>
	40% LLDPE 2045 (1)	65% LDPE 681 (1)
5	40% HDPE 61513.01 (1)	30% LLDPE 2045 (1)
	20% LDPE 681 (1)	5% EVA 3190 (3)
		2 phr FM 1570H (5)

1) Available from The Dow Chemical Company, Midland, Michigan, assignee of the present invention.

10 3) Available from E.I. duPont de Nemours, Wilmington, Delaware.

15 5) A foam concentrate Spectratech FM 1570H, a 50 percent Hydrocerol (sodium bicarbonate/citric acid blend) blowing agent in LDPE concentrate manufactured by Quantum/USI, was utilized at two parts per hundred parts of resin (phr).

		<u>Skin Extruder</u>	<u>Foam Extruder</u>
20	Screw Speed (rpm)	40	80
	Pressure (psig) (kg/cm ²)	3900 (273)	2900 (203)
	Barrel Zone 1 (°C)	171	166
25	Barrel Zone 2 (°C)	182	191
	Barrel Zone 3 (°C)	199	216
	Adapter Zone (°C)	199	210
	Transfer Line (°C)	199	210
30	Melt Temp (°C)	199	212

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	All Die Zones (°C)	199
5	Cast Roll Temp (°C)	32
	Chill Roll Temp (°C)	27
	Line Speed (fpm) (meters/m)	18 (5.5)

10		<u>MD</u>	<u>TD</u>
	Ultimate Tensile Strength psi (kg/cm ²)	2100 (147)	950 (66.5)
	Ultimate Elongatin (%)	515	220
15	2% Segant Modulus (psi) kg/cm ²)	18,400 (1288)	18,7000 (1309)
	Elmendorf Tear Strength (g/mil (0.0254 mm))	25	310

20 Small foam cell size was obtained from the 40 mil (1 mm) gap of the cast film die. Overall, the film exhibits much lower strength and physical properties than blown films with fairly similar composition. The cast film process imparts only mono-directional
25 orientation to the film rather than bi-directional orientation which occurs with a blown or tubular film process. As a result, the physical properties of a cast film are much more unbalanced (MD vs. TD) than those of a blown film.

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Example 6

Several different foam compositions were made into monolayer foamed films at different extruder melt temperatures to determine the effect on foam film

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properties. Film melt extrusion temperatures of 213, 227, 243, and 260°C were utilized. A 100 percent LDPE foam and two different 60 percent LLDPE/35 percent LDPE/5 percent EVA foams were evaluated on a blown film line with a 24:1 L/D 1" (2.54 cm) extruder and a 1-1/4" (3.18 cm) diameter die with a 35 mil (0.9 mm) die gap. 5 Extruder zone temperatures were varied to achieve desired melt temperatures. Other process conditions (extrusion rate, linespeed, film blow-up ratio) were 10 maintained constant.

Increasing melt temperatures caused a dramatic increase in foam cell size, which resulted in decreasing foam density. Higher melt temperatures decrease the 15 polymer melt strength and increase the blowing agent gas pressure-volume, both of which result in larger cell sizes, which in turn causes a reduction in foam density. Foam film physical properties (tensile strength, ultimate elongation, tear strength, and impact strength) 20 were found to significantly decrease in correspondence with the increasing cell size. Foams made at 213°C melt temperature had the smallest cell size, highest foam density and strongest physical properties. Increasing the foam melt temperature from 213°C to 227°C resulted in 25 40 to 75 percent reductions in all physical properties, 19 to 33 percent reduction in foam density, and 130 to 260 percent increase in foam cell size (MD length).

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5 Film A: 100% LDPE 681

10 Film B: 60% LLDPE 4047
 35% LDPE 681
 5% EVA 3190

15 Film C: 60% LLDPE 2045A
 35% LDPE 681
 5% EVA 3190

20 Note: All foam layer composition also contained
 4 phr of Spectratech FM1764L foam concentrate.

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MD Film Properties

<u>Film</u>	<u>Foam Melt Temp (°C)</u>	<u>Avg. Cell Length (mm)</u>	<u>Foam Density (g/cm³)</u>	<u>ULT. Tensile Str. (psi kg/cm²)</u>	<u>ULT. Elong. (%)</u>	<u>El.m. Tear Str. (g/mil 0.0254 mm)</u>	<u>Spencer Impact (g/mil 0.0254 mm)</u>
A (SOLID)	204	0	0.92	3110 (218)	430	50	370
A	213	0.18	0.68	1500 (105)	315	55	199
A	227	0.55	0.55	910 (64)	240	26	128
A	243	0.46	0.46	780 (55)	235	23	103
A	260	1.75	---	355 (25)	170	22	54
B (Solid)	204	0.92	0.92	4600 (322)	730	261	405
B	213	0.71	0.71	1650 (116)	480	280	221
B	227		0.48	900 (63)	370	114	139
B	243	0.48	0.43	475 (33)	340	50	98
B	260	0.43	---	210 (15)	345	37	54

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MD Film Properties

<u>Film</u>	<u>Foam Melt Temp (°C)</u>	<u>AVG. Cell Length (mm)</u>	<u>Foam Density (g/cm³)</u>	<u>ULT. Tensile Str. (psi kg/cm²)</u>	<u>ULT. Elong. (%)</u>	<u>Elm. Tear Str. (g/mil 0.0254 mm)</u>	<u>Spencer Impact (g/mil 0.0254 mm)</u>
C (SOLID)	204	0	0.92	4500 (315)	645	254	478
C	213	0.25	0.61	1200 (84	385	278	193
C	227	0.90	0.41	450 (32)	305	69	110
C	243	1.30	0.39	610 (43)	300	60	112
C	260	2.50	---	240 (24)	310	41	102

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As can be seen from the temperature vs. property data, machine direction (MD) cell lengths of less than 0.6 mm, and preferably less than 0.4 mm, are needed in order to obtain adequate physical properties of a foam film. Although not cited in the above 5 example, transverse (TD) cell widths were always equal to or slightly smaller than the MD length, such that the MD length/TD width ratio was found to be generally 1.0 to 1.4. In both blown tubular and cast flat film 10 processes, the film is predominantly being oriented in the MD direction, so MD cell length is expected to be greater than the TD width.

Example 7

15 Two polyethylene foam compositions were made into blown monolayer films at different extruder melt temperatures and utilizing different blown film die gaps. A 24:1 L/D 1" (2.54 cm) extruder with a 1 to 1/4" 20 (3.18 cm) diameter blown film die (different from that used in Example 6) was constructed with varying diameter inner die mandrels such that four different die gaps (25, 35, 52 and 78 mil) (0.64, 0.89, 1.32 and 1.98 mm) could be obtained. Extruder zone temperatures were 25 adjusted so as to obtain extrusion melt temperatures of 213, 227, 243 and 260°C. All process conditions (extrusion rate, linespeed, film blow-up ratio) were maintained constant; only die configuration (die gap) and zone temperatures (melt temperature) were varied. 30 Resin blends utilized were a 100 percent LDPE and a 40 percent LLDPE - 55 percent LDPE - 5 percent EVA, both with 4 phr of Spectratech FM1764L foam concentrate.

5 Film A: 100% LDPE 681

10 Film B: 55% LDPE 681
 40% LLDPE 2045A
 5% EVA 3190

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The die gap was found to greatly affect foam cell size and thus, the resulting physical properties of the extruded foamed film. At a given melt temperature, increasing the die gap produced a decrease in the extrusion melt back pressure. The resulting foams had larger cell sizes (as shown in the table below) and lower foam density, thus poorer physical properties. As extrusion melt temperature increases, foam properties 20 also deteriorate (as seen in Example 6). Consequently, increasing polymer melt temperature and increasing die gap both have significant adverse affects on foam physical strength properties.

25

With respect to MD tensile strength and elongation, the foam film made with the 35 mil (0.89 mm) gap die exhibits slightly greater properties than does film made with the 25 mil (0.64 mm) gap die. When MD 30 Elmendorf tear strength is evaluated, the 25 mil (0.64 mm) gap produced film is generally slightly stronger. Both die gaps, however, yield foamed film with superior physical properties and smaller cell size than does the 52 (1.32) or 78 mil (1.98 mm) gap dies. Thus, for optimum properties (small cell size, greatest tensile strength, tear strength and ultimate

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elongation), dies with a 25 to 35 mil (0.64 to 0.89 mm) die gap are preferred over larger die gap dies (such as 52 or 78 mil (1.32 or 1.98 mm).

When comparing the physical properties of the
5 LDPE foam film "A" with that of the LLDPE containing
foam "B", the superior strength properties of the LLDPE
containing blend can be readily evidenced by the
significantly greater Elmendorf tear strength values of
the LLDPE blend foam. Increasing the level of LLDPE in
10 the blend will increase the foam film strength
characteristics (assuming that cell size can be kept to
a minimum, preferably below 0.4 mm in MD length).

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<u>Film</u>	<u>Die Gap (mil)</u>	<u>Foam Melt Temp. (°C)</u>	<u>Ultimate Tensile Strength (psi)</u>	<u>Ult. Elong. (%)</u>	<u>Elmen. Tear Strgth. (g/mil)</u>	<u>Avg. MD Cel Length (mm)</u>	<u>Note</u>
A	25	213	1130	270	75	0.2	
A	25	227	1040	240	73	0.3	
A	25	243	815	215	37	0.4	
A	25	260	515	160	33	0.7	
A	35	213	1260	280	78	0.2	
A	35	227	1240	285	24	0.4	
A	35	243	845	250	16	0.5	
A	35	260	460	190	23	0.7	
A	52	213	1170	205	54	0.4	
A	52	227	660	185	31	0.6	MF
A	52	243	810	205	34	0.9	MF, PDC
A	52	260	550	160	27	1.0.	
A	78	213	970	110	44	0.85	MF, PDC
A	78	227	660	135	30	1.7	MF
A	78	243	630	130	21	0.9	MF
A	78	260	465	185	17	1.2	MF

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<u>Film</u>	<u>Die Gap (mil)</u>	<u>Foam Melt Temp. (°C)</u>	<u>Ultimate Tensile Strength (psi)</u>	<u>Ult Elong. (%)</u>	<u>Elmen. Tear Strgth. (g/mil)</u>	<u>Avg. MD Cel Length (mm)</u>	<u>Note</u>
B	25	213	1350	385	193	0.3	
B	25	227	935	340	165	0.3	
B	25	243	465	290	91	0.7	
B	25	260	385	300	59	0.8	
B	35	213	1635	385	113	0.3	
B	35	227	1025	345	110	0.3	
B	35	243	820	320	63	0.7	
B	35	260	600	275	29	1.0	
B	52	213	1240	355	166	0.6	
B	52	227	1035	315	94	0.7	MF
B	52	243	875	300	54	1.0	MF, PDC
B	52	260	380	270	44	1.7	
B	78	227	1085	335	67	0.8	MF, PDC
B	78	243	470	280	34	1.2	MF
B	78	260	355	230	27	1.5	MF

NOTE: MF = Melt Fracture, PDC = Poorly Defined Cells

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The coextruded multilayer foamed films described above are particularly useful for plastic container closure devices of the type disclosed herein. The coextruded multilayer foamed films of the present invention may also be used for density reduction of typical polyolefin films, such as, for example, substrates for silicone coated release liners, for decorative applications, packaging and wrapping films.

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CLAIMS:

1. A 3 to 10 mil (0.08 to 0.25 mm) thick coextruded multilayer foamed film suitable for use for a plastic container closure, the multilayer foamed film having at least one solid polyolefin film layer and at least one foamed polyolefin layer having an average cell size of less than 0.6 millimeters in length.
- 5 2. The multilayer foamed film of Claim 1 wherein the solid polyolefin film layer is a first polyolefin blend containing linear low density polyethylene and low density polyethylene.
- 10 3. The multilayer foamed film of Claim 2 wherein the first polyolefin blend comprises 20 to 90 percent linear low density polyethylene, 10 to 90 percent low density polyethylene, and 0 to 90 percent high density polyethylene.
- 15 4. The multilayer foamed film of Claim 3 wherein the foamed polyolefin layer is a second polyolefin blend containing linear low density polyethylene and low density polyethylene.
- 20 5. The multilayer foamed film of Claim 4 wherein the second polyolefin blend comprises 10 to 90 percent linear low density polyethylene, 10 to 90 percent low density polyethylene, 0 to 50 percent
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ethylene vinyl acetate, and 0 to 30 percent high density polyethylene.

6. The multilayer foamed film of Claim 5 wherein the first polyolefin blend comprises 10 to 80 percent linear low density polyethylene, 10 to 60 percent low density polyethylene, and 0 to 50 percent high density polyethylene and the second polyolefin blend comprises 40 to 75 percent linear low density polyethylene, 20 to 60 percent low density polyethylene, and 2 to 10 percent ethylene vinyl acetate.

7. The multilayer foamed film of Claim 1 wherein the film is a two-ply film having one solid polyolefin film layer and one foamed polyolefin layer.

8. The multilayer foamed film of Claim 7 wherein the solid polyolefin film layer comprises 10 to 40 percent and the foamed polyolefin layer comprises 90 to 60 percent of the total film thickness.

9. The multilayer foamed film of Claim 1 wherein the film is a three-ply film having two outer solid polyolefin film layers and a middle foamed polyolefin layer.

10. The multilayer foamed film of Claim 9 wherein each of the solid polyolefin film layers comprises 5 to 20 percent and the foamed polyolefin layer comprises 90 to 60 percent of the total film thickness.

11. A plastic container closure comprising a threaded or snap-on bottle cap and a liner of a 3 to 10

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mil (0.08 to 0.25 mm) thick coextruded multilayer foamed film of any one of Claims 1 to 10.

12. The plastic container closure comprising a laminate of a 3 to 10 mil (0.08 to 0.25 mm) thick coextruded multilayer foamed film of any one of Claims 1 to 10 having an adhesive joining one surface of said multilayer foamed film to a polyester film and a metallic foil.

13. The plastic container closure of Claim 12 further including a polyester film joined to the other surface of the multilayer foamed film with an adhesive.

14. A method for producing a multilayer foamed film comprising:

15 a) providing a first polyolefin blend and a second polyolefin blend containing a blowing agent,
b) coextruding the first and the second
20 polyolefin blends at a temperature between 204 and 232°C through an extrusion die having a die gap of less than 50 mils (1.27 mm) to form a multilayer extrudate having at least one solid polyolefin film layer formed from the first polyolefin blend and a foamed polyolefin layer
25 formed from the second polyolefin blend having an average cell size of less than 0.6 millimeters in length, and
30 c) cooling the extrudate to form the multilayer foamed film.

15. The method of Claim 18 wherein the first polyolefin blend comprises 20 to 90 percent linear low density polyethylene, 10 to 90 percent low density

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polyethylene, and 0 to 90 percent high density polyethylene.

16. The method of Claim 19 wherein the second polyolefin blend comprises 10 to 90 percent linear low density polyethylene, 10 to 90 percent low density polyethylene, 0 to 50 percent ethylene vinyl acetate, 0 to 30 percent high density polyethylene, and 0.1 to 1.0 percent blowing agent.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/03039

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): B32B 9/00; B29C 65/00 U.S. CL. 428/36.5, 318.6, 318.8, 318.9; 264/45.9, 54																			
II. FIELDS SEARCHED <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="2" style="text-align: center; padding: 2px;">Minimum Documentation Searched ⁷</th> </tr> <tr> <th style="text-align: center; padding: 2px;">Classification System</th> <th style="text-align: center; padding: 2px;">Classification Symbols</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 2px;">U.S.</td> <td style="text-align: center; padding: 2px;">428/36.5, 318.6, 318.8, 318.9 264/45.9, 54</td> </tr> </tbody> </table>		Minimum Documentation Searched ⁷		Classification System	Classification Symbols	U.S.	428/36.5, 318.6, 318.8, 318.9 264/45.9, 54												
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; padding: 2px;">Category ¹⁰</th> <th style="text-align: center; padding: 2px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="text-align: center; padding: 2px;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 2px;">X Y</td> <td style="text-align: center; padding: 2px;">US, A, 4,721,643 (HARAYAMA ET AL) 26 JANUARY 1988; See column 2.</td> <td style="text-align: center; padding: 2px;">1, 9, 10 1, 9, 10</td> </tr> <tr> <td style="text-align: center; padding: 2px;">X Y</td> <td style="text-align: center; padding: 2px;">US, A, 3,819,460 (DUKESS) 25 JUNE 1974 See column 2 and figure 4.</td> <td style="text-align: center; padding: 2px;">1, 7-11 1, 7-11</td> </tr> <tr> <td style="text-align: center; padding: 2px;">Y</td> <td style="text-align: center; padding: 2px;">US, A, 4,022,858 (CAVANNA ET AL) 10 MAY 1977 See Abstract.</td> <td style="text-align: center; padding: 2px;">1-16</td> </tr> <tr> <td style="text-align: center; padding: 2px;">Y</td> <td style="text-align: center; padding: 2px;">US, A, 4,107,247 (DUKESS) 15 AUGUST 1978 See column 3.</td> <td style="text-align: center; padding: 2px;">1-16</td> </tr> <tr> <td style="text-align: center; padding: 2px;">Y</td> <td style="text-align: center; padding: 2px;">US, A, 4,818,577 (OU-YANG) 04 APRIL 1989 See column 2.</td> <td style="text-align: center; padding: 2px;">1-16</td> </tr> </tbody> </table>		Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X Y	US, A, 4,721,643 (HARAYAMA ET AL) 26 JANUARY 1988; See column 2.	1, 9, 10 1, 9, 10	X Y	US, A, 3,819,460 (DUKESS) 25 JUNE 1974 See column 2 and figure 4.	1, 7-11 1, 7-11	Y	US, A, 4,022,858 (CAVANNA ET AL) 10 MAY 1977 See Abstract.	1-16	Y	US, A, 4,107,247 (DUKESS) 15 AUGUST 1978 See column 3.	1-16	Y	US, A, 4,818,577 (OU-YANG) 04 APRIL 1989 See column 2.	1-16
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* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed																			
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family																			
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 2px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; padding: 2px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 2px;">16 JULY 1990</td> <td style="padding: 2px;">01 OCT 1990</td> </tr> <tr> <td style="padding: 2px;">International Searching Authority</td> <td style="padding: 2px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 2px;">ISA/US</td> <td style="padding: 2px;">James J. Seidleck</td> </tr> </table>		Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	16 JULY 1990	01 OCT 1990	International Searching Authority	Signature of Authorized Officer	ISA/US	James J. Seidleck										
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